Concentration of sulfur dioxide from industrial waste-gases
by Robert A Damon

A Thesis Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University

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Under the assumption that certain U. S. smelters expel enough waste SO2 to warrant its commercial recovery, work was undertaken to discover a suitable process for recovering this SO2 and converting it into elemental sulfur. The process' was considered to be twofold: that of concentrating the waste SO2 and that of reducing the concentrated SOg to elemental sulfur. This paper concerns the former.

The objective was to find an absorbent with a high capacity for absorbing SO2, with an ability to be stripped of this SO2, with enough endurance to withstand repeated subjection to stripping temperatures in the vicinity of 100°C without decomposition, and with a resistance to the formation of precipitates during an absorption-desorption cycle.

Of the possible absorbents investigated to solve this problem, the sodium salts of citric, lactic, and malic acids met the above absorbent requirements. The resulting indication of the investigations conducted was that aqueous solutions of the alkali salts of alpha-hydroxy acids that do not yield a precipitate of the acid upon contact with SOg in aqueous solution should serve as satisfactory absorbents for the industrial concentration of SOg from waste gases containing approximately 5% SO2 by volume.

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ABSTRACT

Under the assumption that certain U. S. smelters expel enough waste SO_2 to warrant its commercial recovery, work was undertaken to discover a suitable process for recovering this SO_2 and converting it into elemental sulfur. The process was considered to be twofold: that of concentrating the waste SO_2 and that of reducing the concentrated SO_2 to elemental sulfur. This paper concerns the former.

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Of the possible absorbents investigated to solve this problem, the sodium salts of citric, lactic, and malic acids met the above absorbent requirements. The resulting indication of the investigations conducted was that aqueous solutions of the alkali salts of alpha-hydroxy acids that do not yield a precipitate of the acid upon contact with SO_2 in aqueous solution should serve as satisfactory absorbents for the industrial concentration of SO_2 from waste gases containing approximately 5% SO_2 by volume.

I. Introduction

Substantial quantities of sulfur have been and are still being diluted into the atmosphere, largely in the form of sulfur dioxide, as a direct result of the oxidation of various sulfide ores. This by-product of smelter operations should now be, more than ever before, regarded as a potential source of raw material for the production of elemental sulfur. The following facts will clarify the situation as it now stands:

1. U. S. industry annually consumes vast quantities of sulfur.
2. Since U. S. industry is expanding, the annual demand for sulfur will increase.
3. Discovery of new sulfur deposits has not kept pace with increasing U. S. industrial expansion.

Ninety percent of the world production of elemental sulfur comes from the Frasch-process wells along the Gulf Coast (1). The 1935-39 average yearly production of Frasch sulfur was 2.2 million long tons, and the 1951 production of Frasch sulfur was 5.3 million long tons. Corresponding to these production figures are the consumption figures: 1.4 and 4.8 million long tons, respectively. These figures give an indication of the increasing demands on existing sulfur reserves (2).

Thus, the Gulf Coast Frasch-wells, being the world's largest producers and having the lowest production expenses per ton, control the world sulfur market. However, in 1944, the Gulf Coast had only 60 million long tons of immediately available reserves and 22.2 million long tons of future-available reserves (3). This indicates that the 9, 136 million long tons of by-product sulfur reserves (3) (pyrites, smelter gases, coke-oven gases, etc.) should, in the future, be able to effectively compete with Frasch-produced sulfur and its inevitable price increase brought about by dwindling, harder-to-get-at reserves.

At 1944 operation rates, U. S. smelters would have discharged 20 million long tons of sulfur as diluted SO_2 into the atmosphere in the next 100 years (3). If this sulfur can be recovered at a cost per ton that would enable it to, at the present time, economically compete with Frasch sulfur, it should, in the future, have a decided economic advantage over the latter.

Also, it is forseeable that any process for recovering sulfur from smelter waste-gases can be applied to the recovery of sulfur from pyrites when it becomes economically advantageous to do so. There were 160 million long tons of sulfur reserves as pyrites in the U. S. in 1944 (3).

With these facts in mind, work was undertaken to discover a process for recovering sulfur from waste smelter-gases of approximately 5% SO_2 by volume.

Industrially, the recovery of sulfur can be divided into two steps:

1. Concentration of SO_2 into a relatively pure state.
2. Reduction of the concentrated SO_2 into elemental sulfur.

This investigation was concerned with the first of these steps. The objective was to find an industrially-feasible method which would accomplish the concentration of SO_2 from gases containing dilute SO_2.

Gas absorption was chosen as the physical operation for concentrating the SO_2, and the absorbent-objectives initially set forth were as follows:

1. Find a liquid absorbent with a relatively large capacity for absorbing SO_2.
2. The SO_2-concentrated absorbent must be capable of being stripped of nearly all its SO_2 content.
3. The absorbent must be capable of being recycled with little or no loss of absorbent.

II. Previous Work

A survey of the literature from 1910 through 1954 revealed that the following absorbents had been either commercially or semi-commercially used for the purpose of absorbing SO_2, or suggested for that purpose:

2-amino cymol

di-methyl analine

di-ethylene triamine

tri-ethylene tetramine

quinoline

tetralin

pyridine

analine

xylidine

alkali formate

aluminum sulfite

aluminum sulfate

citrate-phosphate

magnesium sulfite or bi-sulfite

sodium carbonate

ammonium sulfite

ammonium thiocyanate

silica gel

alkali hydroxide

ammonium hydroxide

The major difficulty with processes using various of the above-mentioned absorbents, was the loss of absorbent through vaporization or through formation of by-products which occur as precipitates.

Some by-products such as ammonium sulfate, resulting when ammonia is used as an absorbent, are easily marketable, while others such as calcium sulfate are not easily marketable. In order that these handicaps might be eliminated, item #3 of the aforementioned absorbent-objectives was stipulated.

Howat (4), in 1940, summarized the work that had been done on SO_2 absorption. He stated that the capacity of a given solution for absorbing SO_2 is inversely proportional to the square of the hydrogen-ion concentration. Large quantities of SO_2 may be dissolved in alkaline solutions, but regeneration of the SO_2 by heating then becomes almost impossible. Howat's calculations revealed that solutions with pH less than 3.5 will not dissolve sufficient SO_2 and that solutions with pH greater than 3.5 do not favor easy regeneration of SO_2 by heating.

III. Plan of Investigations

To predict the behavior of any absorbent under operating conditions, equilibrium data for the gas-absorbent system is necessary. Determination of operating conditions and column design are impossible without this information.

Equilibrium data for the absorbents considered during this investigation were not available in the literature; thus, a three-phase research plan was instigated:

1. Determine equilibrium data for a series of possible absorbents.
2. Determine the ease and completeness of stripping SO_2

from these absorbents.

3. With the aid of the above information, eliminate the undesirable absorbents and study the desirable absorbents under simulated large-scale operating conditions on laboratory scale in a continuous-absorption column.

IV. Absorbents Investigated Under Steps 1 and 2 of the Plan of Investigations

Each absorbent was allowed to reach a state of equilibrium with a series of SO_2-air mixtures in the absorption apparatus pictured in Figure 10. The quantity of SO_2 in any given absorbent was determined by titration. When points representing SO_2 concentration in an absorbent vs. SO_2 concentration of the SO_2-air mixture in equilibrium with the absorbent, were plotted, an equilibrium curve for that particular absorbent resulted.

The ability of an absorbent to be stripped of its SO_2 content was determined by maintaining the absorbent at 90°C and periodically titrating samples of the absorbent until the SO_2 content had attained a minimum value.

During the absorption and desorption determinations, particular attention was directed toward the formation of any by-products or decomposition products. If either of these appeared, they were analyzed and their significance evaluated.

Equilibrium data and curves for the following absorbents appear at the end of this section.

A. Sodium Formate

A recent Japanese patent had been secured on the use of alkali formate as an absorbent for SO_2, but no equilibrium data was available. It was decided to determine equilibrium data for aqueous sodium formate solutions of increasing concentration. This would show the nature of equilibrium for a successful absorbent and also show the behavior of equilibrium as the concentration of the absorbent was increased.

Data was obtained for solutions of 10, 20, and 30 grams of sodium formate per 100 grams of water. Absorption was successful and was found to be more effective as the concentration of sodium formate was increased. The 20 pbw solution was 1.15 times as effective as the 10 pbw solution, and the 30 pbw solution was 1.5 times as effective as the 10 pbw solution. This increase in effectiveness is, of course, limited by the maximum solubility of a given salt in water. Hence, it was decided to use a 50 pbw solution (an average within the limits of maximum solubility for the salts of most organic acids) when studying other possible absorbents.

Although sodium formate proved a good absorbent for SO_2, it did not satisfactorily meet the absorbent requirements set forth initially. Upon heating to set free the absorbed SO_2, a colloidal precipitate appeared. This occurrence held true for each pbw solution studied. The precipitate was soluble in carbon disulfide, and, upon evaporation of the carbon disulfide, yellow crystals, identifiable as sulfur, appeared. The mechanism for this reaction was proposed as follows (reaction mechanisms are discussed more fully in a later section):

1. $SO_2 + H_2O \longrightarrow 2H^+ + SO_3^=$
2. $HCOONa \longrightarrow HCOO^- + Na^+$
3. $H^+ + HCOO^- \longrightarrow HCOOH$
4. $2Na^+ + SO_3^= \longrightarrow Na_2SO_3$
5. $2HCOOH + Na_2SO_3 \longrightarrow 2NaHCO_3 + S\downarrow + H_2O$

B. <u>Sodium Chloride</u>

Sodium chloride, alone not satisfactory for absorbing and recovering SO_2, was buffered to a pH 3.5 with concentrated HCl in order to improve the desorption characteristics of the solution. Equilibrium data was obtained for a 35 pbw aqueous NaCl solution buffered to pH 3.5.

It proved to be a very poor absorbent for SO_2, absorbing approximately 0.001 mols SO_2/mol absorbent, for a 5% SO_2 inlet gas. Desorption characteristics were such that there could be no possible recovery of SO_2 by desorption unless an inlet gas containing greater than 17.5% SO_2 by volume were used.

C. Glycine

A 20 pbw aqueous solution of glycine was used as an absorbent. Absorption capacity for a 5% SO_2 inlet gas was 0.007 mols SO_2/mol absorbent. For recovery of SO_2 by desorption, however, an inlet gas of greater than 9% SO_2 would be required.

D. Sodium Citrate

A 50 pbw aqueous sodium citrate solution was studied. Equilibrium with 5% SO_2 inlet gas was 0.0435 mols SO_2/mol absorbent. After desorption, the solution contained 0.0136 mols SO_2/mol absorbent. No precipitates or undesirable by-products occurred during absorption or desorption.

E. Sodium Benzoate

A 50 pbw aqueous sodium benzoate solution was studied. However, a very heavy precipitate of benzoic acid crystals occurred during the absorption, thus rendering sodium benzoate an undesirable absorbent.

F. Sodium Salicylate

The 50 pbw aqueous solution of sodium salicylate studied proved to have a low absorption capacity for SO_2;

0.0044 mols SO_2/mol absorbent with a 5% SO_2 inlet gas. After desorption, however, the solution contained only 0.00183 mols SO_2/mol absorbent. Thus, a small amount of recovery is possible from a 5% SO_2 inlet gas. A small amount of salicylic acid was precipitated during absorption, but this redissolved during desorption.

G. n-Butyl and n-Hexyl Amines

A preliminary test by Orsat analysis on aqueous solutions of the above amines revealed that their absorption capacity for SO_2 was exceedingly small.

Absorption equilibria were not found for the amines because a successful titration could not be carried out in order to analyze the amines for SO_2 content:

absorption:

$$RNH_2 \xrightarrow[H_2O]{SO_2} RNH_2.SO_2$$

proposed titration:

$$RNH_2 + RNH_2 . SO_2 \xrightarrow{HA} RNH_2 . HA + RNH_2 . SO_2$$

actual titration results:

$$RNH_2 + RNH_2 . SO_2 \xrightarrow{HA} 2RNH_2 . HA + SO_2$$

H. Cyclo-pentadiene

Cyclo-pentadiene was tried as an absorbent. The supposed reaction was that SO_2 would add to the cyclo-pentadiene molecule by 1-4 addition. Solvent loss, however, was so great that cyclo-pentadiene was abandoned as unfeasible.

I. Sodium Tartrate

Equilibrium data was obtained for a 50 pbw aqueous solution of sodium tartrate. This solution had a good absorption capacity for SO_2: 0.01950 mols SO_2/mol absorbent for a 5% SO_2 inlet gas. The SO_2 content after desorption was 0.00308 mols SO_2/mol absorbent. A moderate amount of tartaric acid was precipitated during absorption, but it redissolved during desorption.

K. Sodium Malate

Sodium malate also exhibited a good absorption capacity for SO_2. A 50 pbw aqueous solution of sodium malate in equilibrium with 5% SO_2 inlet gas held 0.0192 mols SO_2 /mol absorbent. After desorption, the SO_2 content was 0.00643 mols SO_2/mol absorbent. No precipitate was observed during absorption or desorption.

V. Absorption Reaction-Mechanisms

The following facts led to the proposed mechanism for the reaction of the sodium salt of an organic acid with SO_2 in aqueous solution:

1. Hydrogen ions were formed and the organic acid, originally present as its sodium salt, was a product.

2. Small amounts of SO_2 in the presence of excess sodium-salt-of-the-acid rendered the absorption kinetics extremely sensitive to even a small variation in the amount of SO_2 available for absorption.

3. The acid products were vastly more soluble in water at 90°C than in water at 25°C.

The proposed mechanism was:

1. $H_2O + SO_2 \rightleftharpoons 2H^+ + SO_3^=$

2. $ANa \rightleftharpoons A^- + Na^+$

3. $A^- + H^+ \rightleftharpoons AH$

4. $2Na^+ + SO_3^= \rightleftharpoons Na_2SO_3$

Sodium sulfite is nearly twice as soluble in water at 90°C as in water at 25°C, and the acids investigated were insoluble or slightly soluble at 25°C and very soluble at 90°C. This would tend to aid a reversal of the above mechanism during desorption. The reversal of reaction #1 is also favored by increased temperature.

The sodium salts of citric, tartaric, lactic, and malic acids were found to be exceptionally good absorbent media for SO_2. All of these acids are alpha hydroxy. The influence of this alpha hydroxyl group seemed to be executed in such a manner that the dissociation constant of the acid was near $10^{-3.5}$ as suggested by Howat (4). In other words, the sodium salts of alpha hydroxy acids are capable of absorbing sufficient quantities of SO_2 and yet are capable of easily releasing this SO_2 upon heating.

For the key reaction:

$$SO_2 + H_2O \rightleftharpoons SO_3^{=} + 2H^+$$

K_{eq} was calculated from delta-H and delta-F of the reaction.

$273^\circ K$: $K_{eq} = 8.7 \times 10^{-9}$

$298^\circ K$: $K_{eq} = 1.9 \times 10^{-9}$

$323^\circ K$: $K_{eq} = 4.9 \times 10^{-10}$

Thus, the reaction is favored by decreasing temperature.

Values of K_N were calculated for this reaction at various pressures.

where: $$K_N = \frac{(N_{H^+})^2 \, (N_{SO_3^=})}{(N_{H_2O}) \, (N_{SO_2})} = \frac{K_{eq}}{K_r \cdot P^{\Delta n}}$$

N = mol fraction

The calculated results for K_N at $298^\circ K$ and various pressures were:

1 atm: $K_N = 1.65 \times 10^{-9}$

50 atm: $K_N = 5.12 \times 10^{-11}$

100 atm: $K_N = 5.48 \times 10^{-14}$

Thus, increased pressure does not favor an increased concentration of $SO_3^{=}$ and H^+ ions. The small fluctuation of pressure (640±5 mm Hg) during the collection of equilibrium data should not have had any adverse effect on the accuracy of the equilibrium determinations.

VI. Continuous Runs

Those absorbents that gave satisfactory results for phases #1 and #2 of the plan of investigations were subjected to a 20-hour test run in the continuous-absorption setup pictured in Figure 11. The sodium salts of citric, tartaric, malic, lactic, and salicylic acids were considered for subjection to continuous run analysis, but the net absorption capacity of sodium salicylate was regarded as too small for sodium salicylate to be included in the actual test runs.

The purpose of the test runs was twofold:

1. To see if the absorbent under consideration would maintain its absorption-desorption characteristics over a 20-hour period (regarded by the author as a sufficient endurance test) without any decomposition or formation of precipitated by-products occurring.
2. To check the accuracy of the equilibrium curves (the operating line, determined from the slope of the equilibrium curve will not yield predicted results if the equilibrium curve is more than moderately in error).

Sodium lactate, sodium citrate, and sodium malate were found satisfactory for possible industrial use as absorbents for SO_2 recovery. Sodium tartrate, however, could not be fully tested in the continuous-absorption apparatus. Large amounts of tartaric acid were precipitated during the test run. This caused clogging of the pumps and column, making further testing impossible.

The tests indicated that lactate, citrate, and malate should withstand industrial use at desorption temperatures of 100°C and absorption temperatures of 25°C.

The test results also gave evidence that the absorption curves were reasonably accurate. However, for accurate industrial calculations, the author suggests that the region of the curves from $y=0$ to $y=0.06$ be more accurately determined by using flow meters with greater sensitivity at low flow rates than were at the disposal of the author.

These absorbents recovered approximately 96% of the SO_2 in the gas passed through the absorption column. As far as low pumping costs are concerned, the absorbents should be ranked in the order citrate $<$ lactate $<$ malate, the order being determined by the equilibrium-curve slopes.

The accuracy of the equilibrium curves was determined in the following manner:

The lower terminal of the operating line for each absorbent was picked to nearly coincide with the equilibrium curve at a gas outlet-composition of $y_2 = 0.002$. The operating conditions were then set so that the operating line closely paralleled the equilibrium curve. A value was predicted for x_1 as determined by the intersection of the operating line with $y_1 = 0.05$, the inlet gas-composition. If the experimental y_2-value was radically greater than $y = 0.002$, the implication would be that the curve crossed the operating line at a y-value of less than the inlet gas-composition or, in other words, the slope of the equilibrium curve was greater than thought to be. If the value predicted for x_1 checked closely with the experimental results, the slope of the equilibrium curve was either less than thought to be or as originally determined.

The equilibrium-curve slopes used for determining the operating lines were picked as steep as possible, within the limits of reasonable extrapolation. If the experimental evidence did not show that the equilibrium curve crossed over the operating line, the curve was then thought to be satisfactory. Small values for the slope of the equilibrium curve are desirable, for, as the slope approaches a 0 value, the absorption capacity approaches the infinite and the liquor-to-gas ratio approaches a value of 0.

VII. Experimental Methods

A. Determination of Equlibrium Curves

As stated in the plan of investigations, the first step was to determine equilibrium data for a series of possible absorbents. Figure 10 is a diagram of the apparatus and accessories used to obtain this information.

Air and SO_2 were metered by means of manometers through a series of mixing orifices into a mixing flask. From this flask, the gas mixture passed through a glass tube, tipped with sintered glass and immersed in the absorbent being investigated. The gas mixture emerged from the sintered-glass tip in the form of minute bubbles. The bubbles, rising up the narrow section of the absorption flask, created turbulent mixing of the gas mixture and absorbent, and thus provided efficient contacting of the two.

The condenser, through which the exhaust gas-mixture passed, provided a means for removing entrained absorbent. The absorbent temperature was maintained at 25°C with a water bath. Pressure was that of the atmosphere, being an average 640 mm Hg. Pressure does not exert a great amount of influence on the absorption of SO_2 in aqueous solutions.

For a gas mixture with a given SO_2 composition, the absorbent was titrated periodically until a constant titration value was attained. The amount of SO_2 in the absorbent at constant titration was the amount in equilibrium with the specified gas-mixture in contact with the absorbent. The gas mixture was analyzed by means of an Orsat.

The above procedure was repeated for various specified gas-mixtures to give equilibrium points representing an equilibrium curve.

B. Continuous Runs

Those absorbents that were predicted suitable for absorption of SO_2 were studied in the continuous absorption-desorption apparatus pictured in Figure 11.

Two 36" x 1" glass columns packed with glass rings were used, one for absorption and the other for desorption.

Absorbent, stripped of its SO_2 content and at 25°C, was pumped into the top of the absorption column and allowed to trickle down the column at a predetermined rate. An air-SO_2 mixture (5% SO_2) was fed into the bottom of the column, counter-current to the absorbent flow. The gas mixture, being relieved of its SO_2 content during its traverse of the column, was passed through a condenser to remove any entrained absorbent and then analyzed for SO_2 by the Orsat method.

The SO_2-concentrated absorbent discharged from the absorption column was collected and fed into a desorption column which was maintained at 100°C. In this column, SO_2 was stripped from the absorbent and passed through a condenser. The gas leaving the condenser was concentrated SO_2. The stripped absorbent was then pumped through a heat exchanger and back to the absorption column. Analysis of the concentrated and stripped absorbents was accomplished by titration.

C. Method of Titration

A known amount of absorbent was placed in an Orsat pipette and caused to absorb a given volume of SO_2, as measured by the Orsat. This solution was then titrated with a standardized NaOH solution to give a titration constant:

$$K_{titr} = \frac{\text{ml NaOH}}{\text{mol } SO_2}$$

When an absorbent containing an unknown amount of SO_2 was titrated:

$$\text{titration value} = \text{ml NaOH/ml absorbent}$$

then:

$$\frac{\text{mols } SO_2}{\text{ml absorbent}} = \text{titration value}/K_{titr}$$

$$\frac{\text{mols } SO_2}{\text{mols absorbent}} = \frac{\text{titration value}}{K_{titr}} \times \frac{\text{ml absorbent}}{\text{mol absorbent}}$$

The K_{titr} for each absorbent was checked and verified in order to obtain a value with little or no deviation over the range of SO_2 concentration that applied to each absorbent.

D. Discussion of Experimental Errors

Orsat gas-analysis is accurate to ± 0.001 for y-values if 100-cc gas-samples at room temperature are used. Repeated analyses of a given gas-sample were duplicable within these values.

Because of the care taken to verify the titration constant, the error in SO_2-concentration values determined by titration should have been only that error governed by the reading accuracy of the 50-ml burettes used for titrating.

The author was not able to obtain reproducible points on the equilibrium curves in the region from $y = 0$ to $y = 0.06$. However, points representing y-values above this region were reproducible. The unreproducible region, being only a small part of the total curve, was extrapolated to the origin as determined by the characteristics of the known curve. That the extrapolations were sufficiently accurate was corroborated by the results of the continuous runs. The reasons for lack of reproducible results in the region stated above were believed to be:

1. Since the absorption was predominently chemical and not physical, the greater concentration of absorbent compared to SO_2 concentration in this region, would have made SO_2 concentration the controlling factor.

2. The manometers used for metering the SO_2-air mixture were not capable of maintaining a constant SO_2 concentration in this region.

Thus, since the SO_2 concentration is more directly controlling in this region than in any other, and since the manometers could not hold the SO_2 concentration sufficiently constant in this region, the results were not reproducible. However, this difficulty had little effect on the net experimental results.

Summary

Sodium formate, sodium chloride buffered to pH 3.5, glycine, sodium citrate, sodium benzoate, sodium salicylate, n-butyl amine, n-hexyl amine, cyclopentadiene, sodium tartrate, sodium lactate, and sodium malate were investigated as possible industrial absorbents for concentrating SO_2 from waste gases of approximately 5% SO_2 by volume.

Their absorption-desorption characteristics were studied, and equilibrium data at 25°C was determined for those absorbents where this was possible. Those which gave evidence of being industrially feasible as absorbents for SO_2 were subjected to study in a continuous absorption-desorption apparatus at temperatures of 25 and 100°C, respectively.

The sodium salts of citric, lactic, and malic acids were the only members of the above group of absorbents investigated that proved entirely satisfactory.

Nomenclature

L = liquid flow rate

G = gas flow rate

M = slope of equilibrium curve

L/G = slope of operating line

T_A = absorption temperature

T_D = desorption temperature

X = mols SO_2/mol absorbent

X_1 = absorption column liquid-outlet composition, mols SO_2/mol absorbent

X_2 = absorption column liquid-inlet composition, mols SO_2/mol absorbent

Y = mols SO_2/mol gas

Y_1 = absorption column gas-inlet composition, mols SO_2/mol gas

Y_2 = absorption column gas-outlet composition, mols SO_2/mol gas

TABLE I

EQUILIBRIUM DATA

A. Absorbent: a 10 pbw aqueous Sodium Formate solution
Gas: air-SO_2 mixture

x	y
0.0231	0.06
0.0253	0.132
0.0275	0.249
0.0284	0.390

Desorption: absorbent decomposed

B. Absorbent: a 20 pbw aqueous Sodium Formate solution
Gas: air-SO_2 mixture

x	y
0.0268	0.06
0.0288	0.132
0.0311	0.249
0.0322	0.390

Desorption: absorbent decomposed

C. Absorbent: a 30 pbw aqueous Sodium Formate solution
Gas: air-SO_2 mixture

x	y
0.0361	0.06
0.0376	0.132
0.0406	0.249
0.0410	0.390

Desorption: absorbent decomposed

TABLE I - continued

EQUILIBRIUM DATA

D. Absorbent: a 35 pbw aqueous Sodium Chloride solution, buffered with HCl to an initial pH at 3.5.
Gas: air-SO_2 mixture

x	y
0.00120	0.06
0.00269	0.132
0.00582	0.249
0.00990	0.390

Desorption: x = 0.004

E. Absorbent: a 20 pbw aqueous Glycine solution
Gas: air-SO_2 mixture

x	y
0.0080	0.06
0.0132	0.132
0.0174	0.249
0.0205	0.390

Desorption: x = 0.01075

F. Absorbent: a 50 pbw aqueous Sodium Citrate solution
Gas: air-SO_2 mixture

x	y
0.0470	0.076
0.0517	0.132
0.0561	0.249
0.0622	0.390

Desorption: x = 0.0136

TABLE I - continued

EQUILIBRIUM DATA

G. Absorbent: a 50 pbw aqueous Sodium Salicylate solution
Gas: air-SO_2 mixture

x	y
0.00521	0.076
0.00544	0.132
0.00574	0.249
0.00582	0.390

Desorption: x = 0.00183

H. Absorbent: a 50 pbw aqueous Sodium Tartrate solution
Gas: air-SO_2 mixture

x	y
0.02355	0.0983
0.0250	0.132
0.0275	0.249
0.0309	0.390

Desorption: x = 00308

I. Absorbent: a 50 pbw aqueous Sodium Lactate solution
Gas: air-SO_2 mixture

x	y
0.0224	0.094
0.0253	0.142
0.0257	0.242
0.0266	0.380

Desorption: x = 0.00946

TABLE I - continued

EQUILIBRIUM DATA

J. Absorbent: a 50 pbw aqueous Sodium Malate solution
Gas: air-SO_2 mixture

x	y
0.01695	0.068
0.0368	0.142
0.0381	0.250
0.0442	0.380

Desorption: $x = 0.00643$

TABLE II - CONTINUOUS RUN DATA FOR SODIUM LACTATE

Average of Hourly Readings	Y_1	Y_2	X_2	X_1	T_D °C	T_A °C
1st 4 hr	0.05	0.001	0.0052	0.0132	100	23
2nd 4 hr	0.048	0.002	0.00620	0.0135	100	23
3rd 4 hr	0.048	0.002	0.00536	0.0134	100	24
4th 4 hr	0.046	0.002	0.00587	0.0138	100	25
5th 4 hr	0.044	0.002	0.00620	0.0136	100	28

Absorbent: 50 pbw aqueous solution of Sodium Lactate.

Operating Conditions:

$M = 2.86$ (avg. from $y = 0$ to $y = 0.06$)

$L/G = 4.08$

G (air) = 0.1653 Std. cu. ft./min.

G (SO_2) = 0.0087 Std. cu. ft./min.

L = 20 ml/min. = 0.9 gm. mols/min.

Results:

% SO_2 recovery: 96.3%

21.7 gm. SO_2 recovered/liter absorbent circulated.

No decomposition of absorbent over 20-hr. run.

TABLE III - CONTINUOUS RUN DATA FOR SODIUM MALATE

Average of Hourly Readings	Y_1	Y_2	X_2	X_1	T_D °C	T_A °C
1st 4 hr	0.045	0.002	0.0145	0.0215	100	25
2nd 4 hr	0.045	0.002	0.0152	0.0227	100	25
3rd 4 hr	0.048	0.002	0.0135	0.0211	100	23.3
4th 4 hr	0.048	0.002	0.0127	0.0203	101	23
5th 4 hr	0.046	0.002	0.0104	0.0205	102	27.8

Absorbent: a 50 pbw aqueous solution of Sodium Malate.

Operating Conditions:

$M = 3.34$ (avg. from $y = 0$ to $y = 0.06$)

$L/G = 4.77$

G (air) = 0.1292 Std. cu. ft./min.

G (SO_2) = 0.0068 Std. cu. ft./min.

L = 20 ml/min. = 0.812 gm-mols/min.

Results:

% SO_2 recovery: 95.7%

20.6 gm SO_2 recovered/liter absorbent circulated.

No decomposition of absorbent over 20-hr. run — light ppt. of Malic acid that redissolved during desorption.

TABLE IV - CONTINUOUS RUN DATA FOR SODIUM CITRATE

Average of Hourly Readings	Y_1	Y_2	X_2	X_1	T_D °C	T_A °C
1st 4 hr	0.044	0.0015	0.0154	0.0262	100	25
2nd 4 hr	0.046	0.0015	0.0164	0.0296	99	28
3rd 4 hr	0.048	0.002	0.0172	0.0308	99	28.5
4th 4 hr	0.045	0.002	0.0165	0.0296	100	28
5th 4 hr	0.049	0.002	0.0151	0.0286	100	26

Absorbent: a 50 pbw aqueous solution of Sodium Citrate.

Operating Conditions:

M = 2.515 (avg. from $y = 0$ to $y = 0.06$)

L/G = 3.59

G (air) = 0.1506 Std. cu. ft./min.

G (SO_2) = 0.00792 Std. cu. ft./min.

L = 15 ml/min. $\doteq$ 0.717 gm-mols/min.

Results:

% SO_2 recovery: 95.8%

38.6 gm. SO_2 recovered/liter absorbent circulated.

No decomposition of absorbent over 20-hr. run.

REFERENCES:

(1) Shreve, Chemical Process Industries, McGraw-Hill, 1955, p. 354.

(2) 1951 Minerals Yearbook, U. S. Bureau of Mines.

(3) Mineral Resources of the U. S., Public Affairs Press, Washington, D. C.

(4) Howat, The Chemical Age, 43, 249-75 (1940).

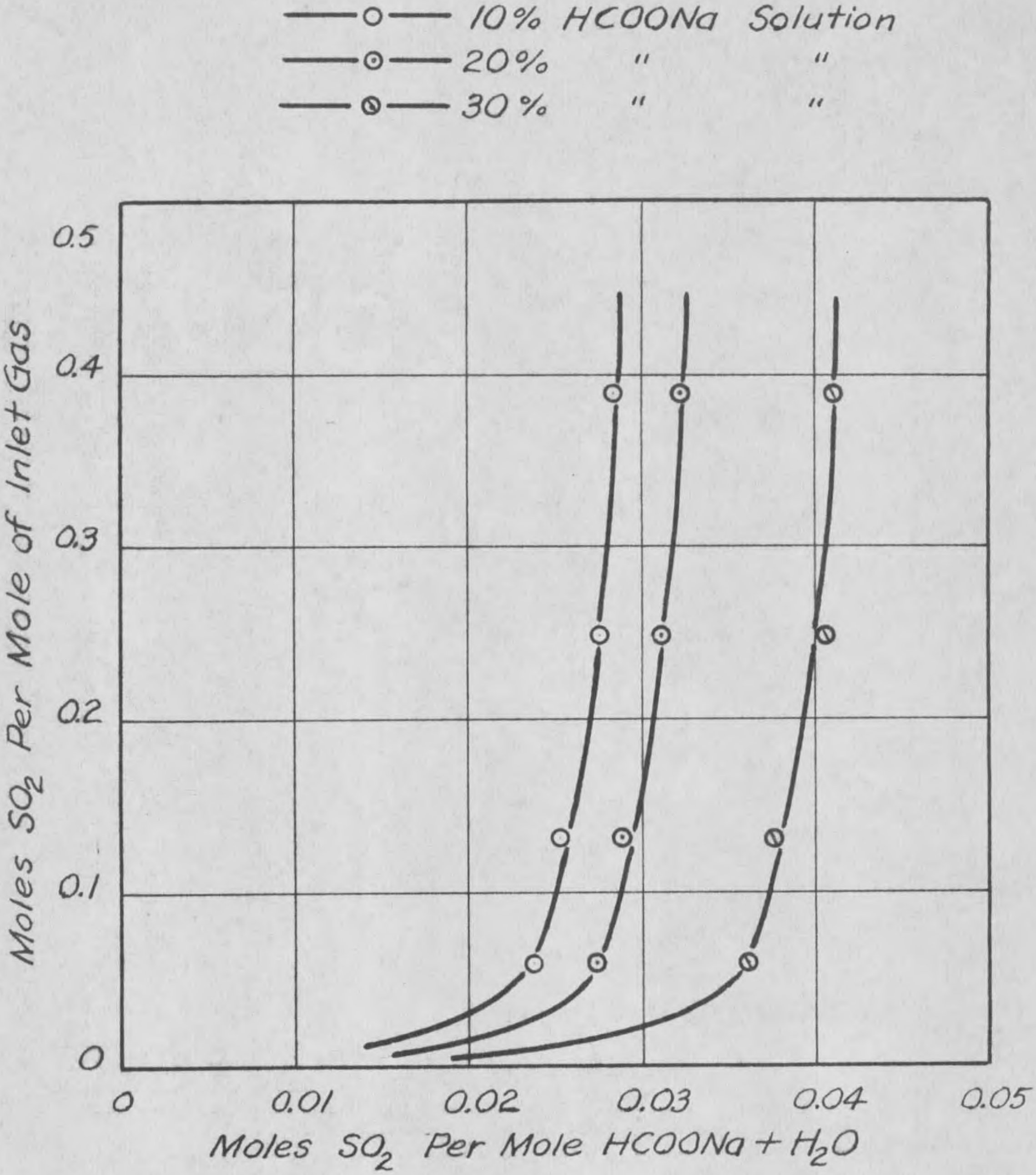

Figure 1. Equilibrium curves of sodium formate.

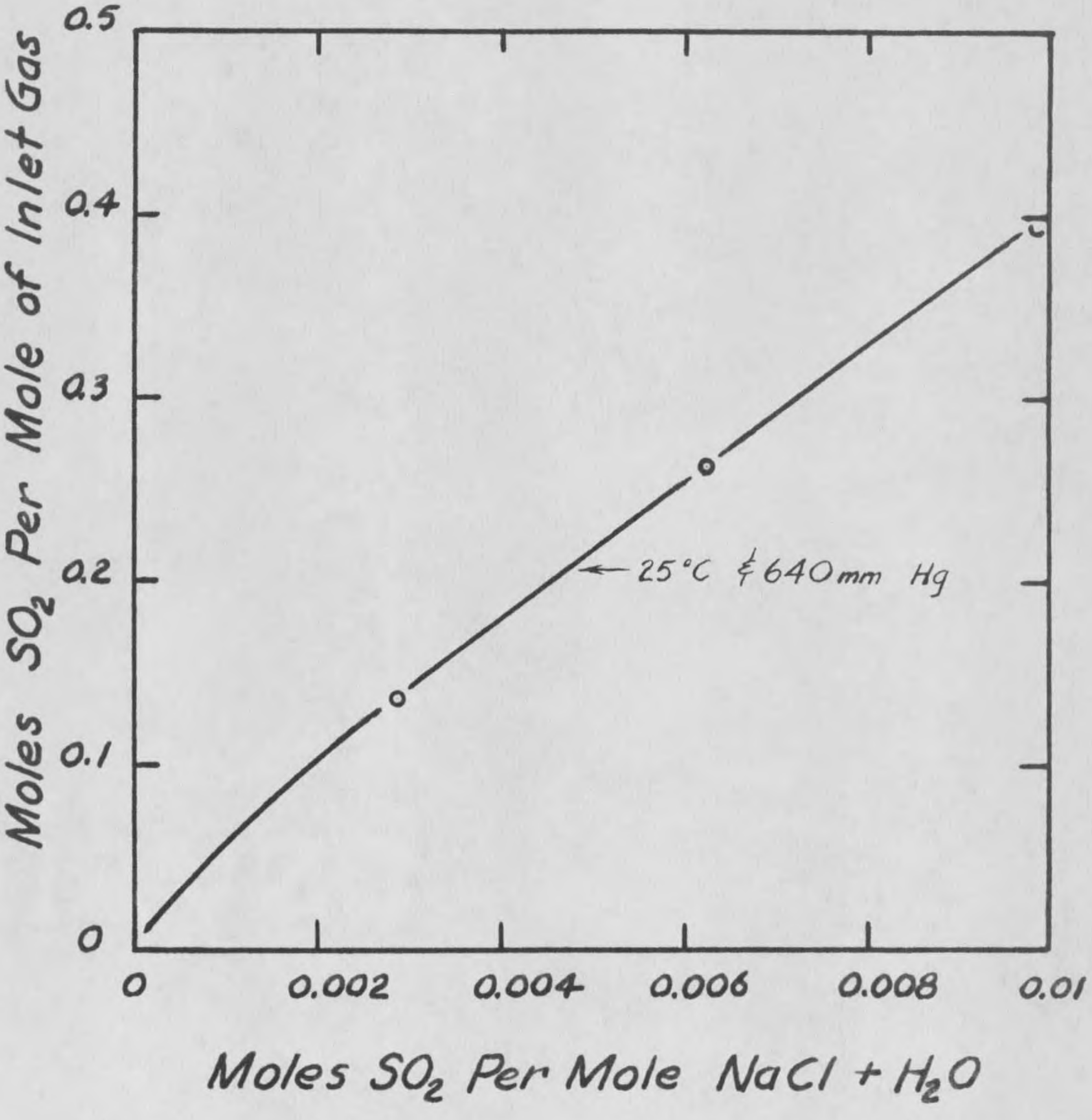

Figure 2. Equilibrium curve of sodium chloride.

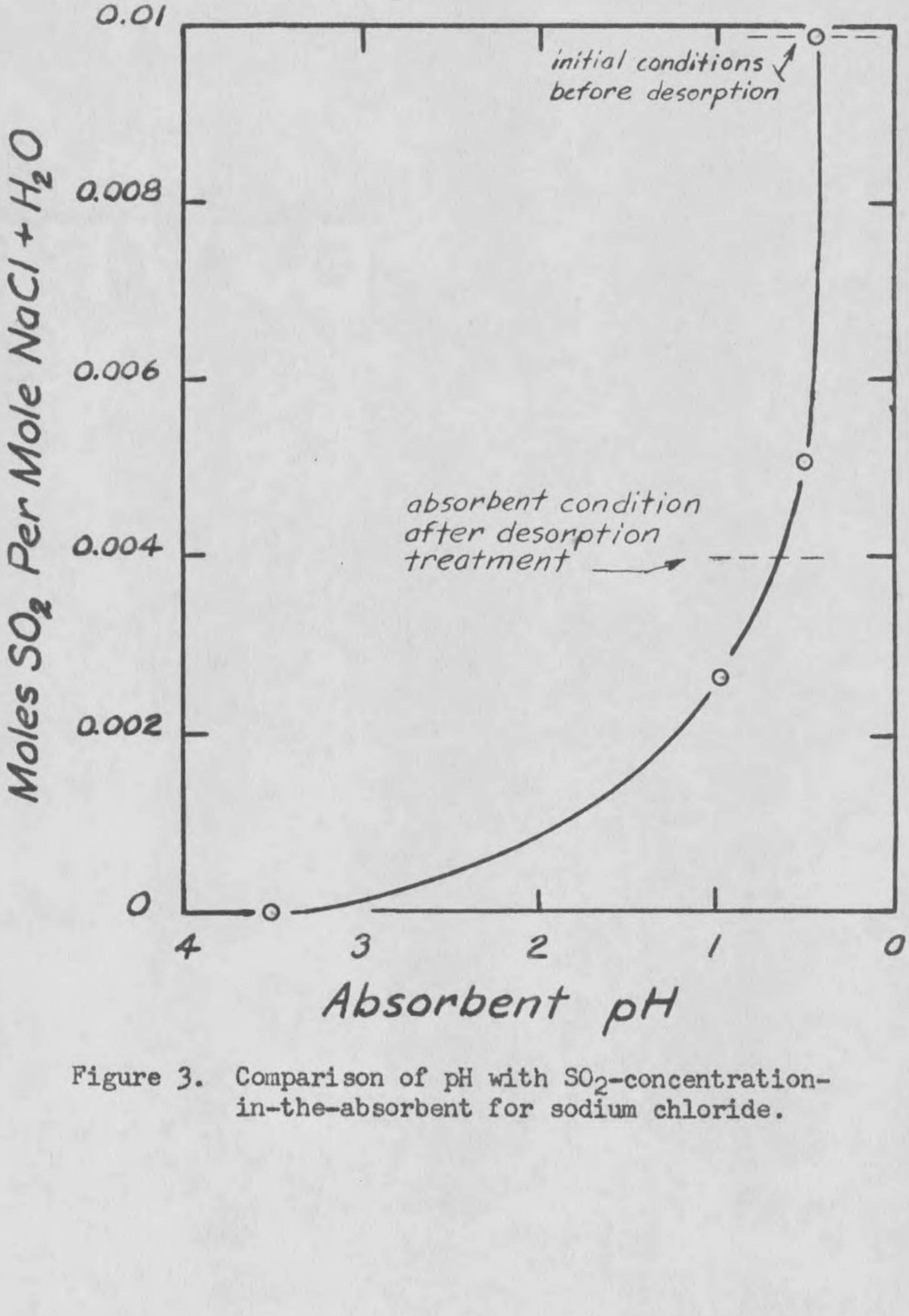

Figure 3. Comparison of pH with SO_2-concentration-in-the-absorbent for sodium chloride.

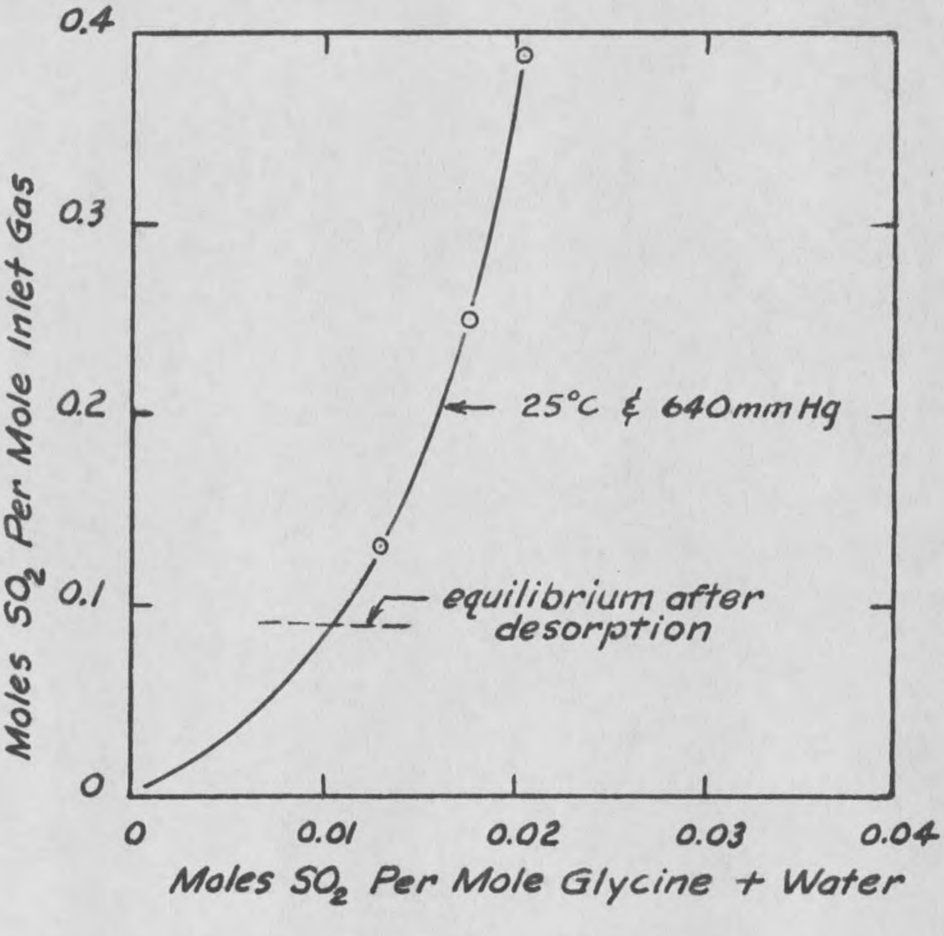

Figure 4. Equilibrium curve of glycine.

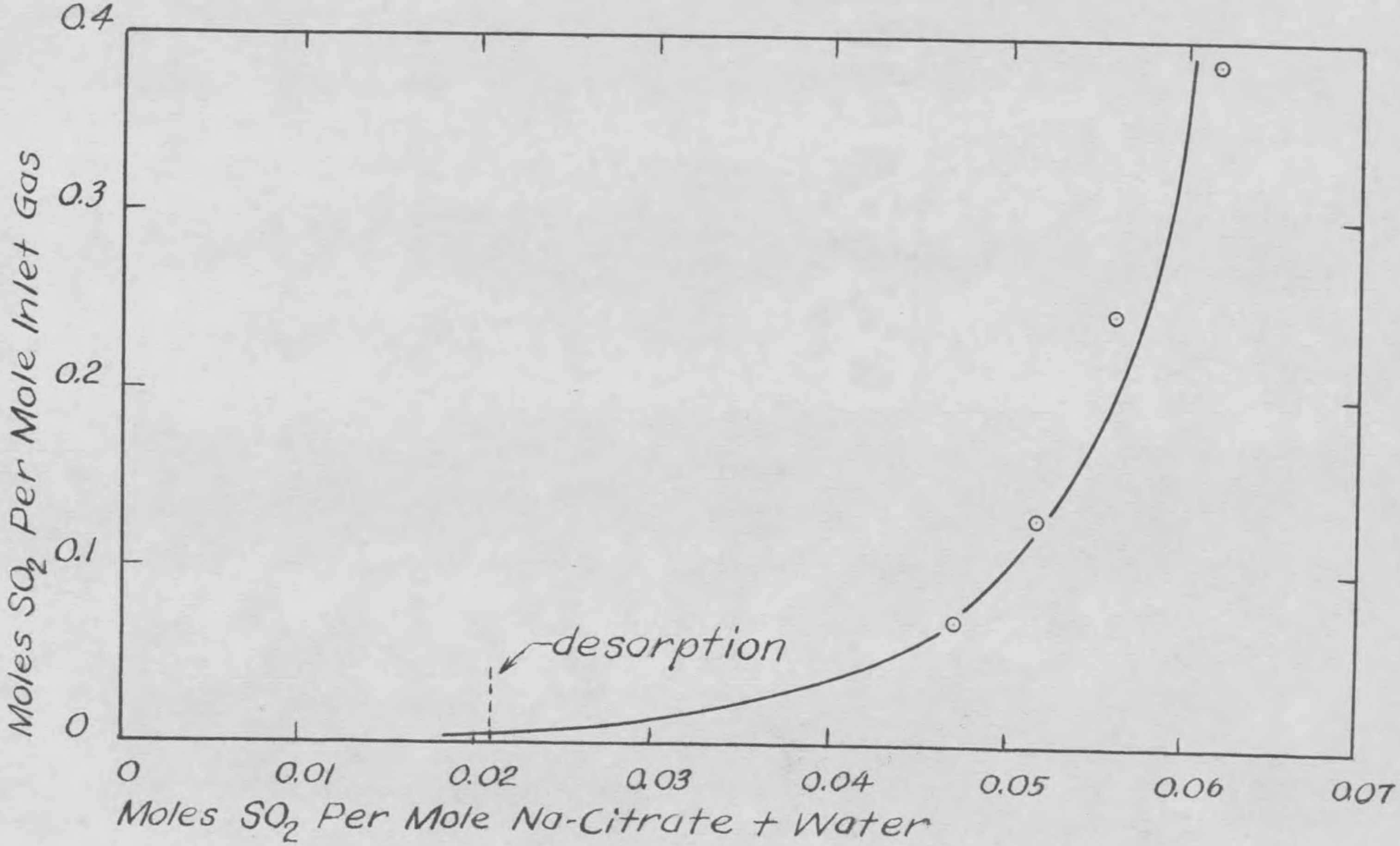

Figure 5. Equilibrium curve of sodium citrate.

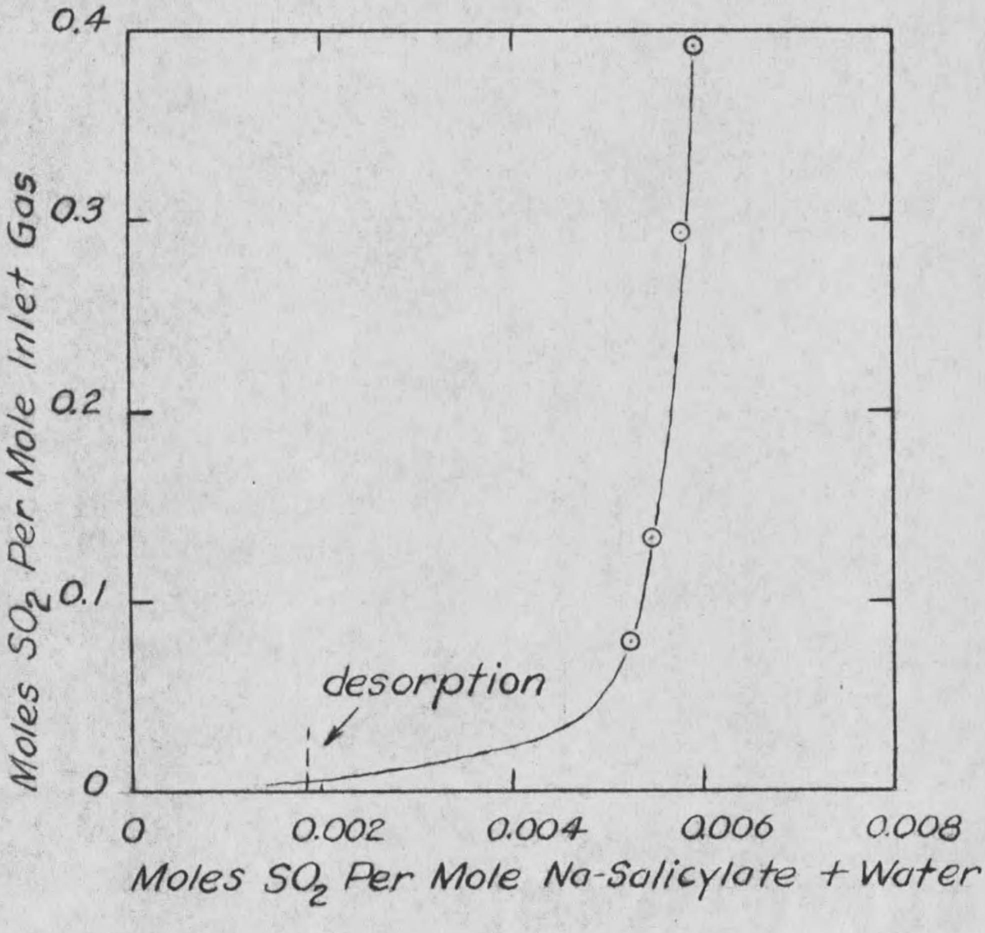

Figure 6. Equilibrium curve of sodium salicylate.

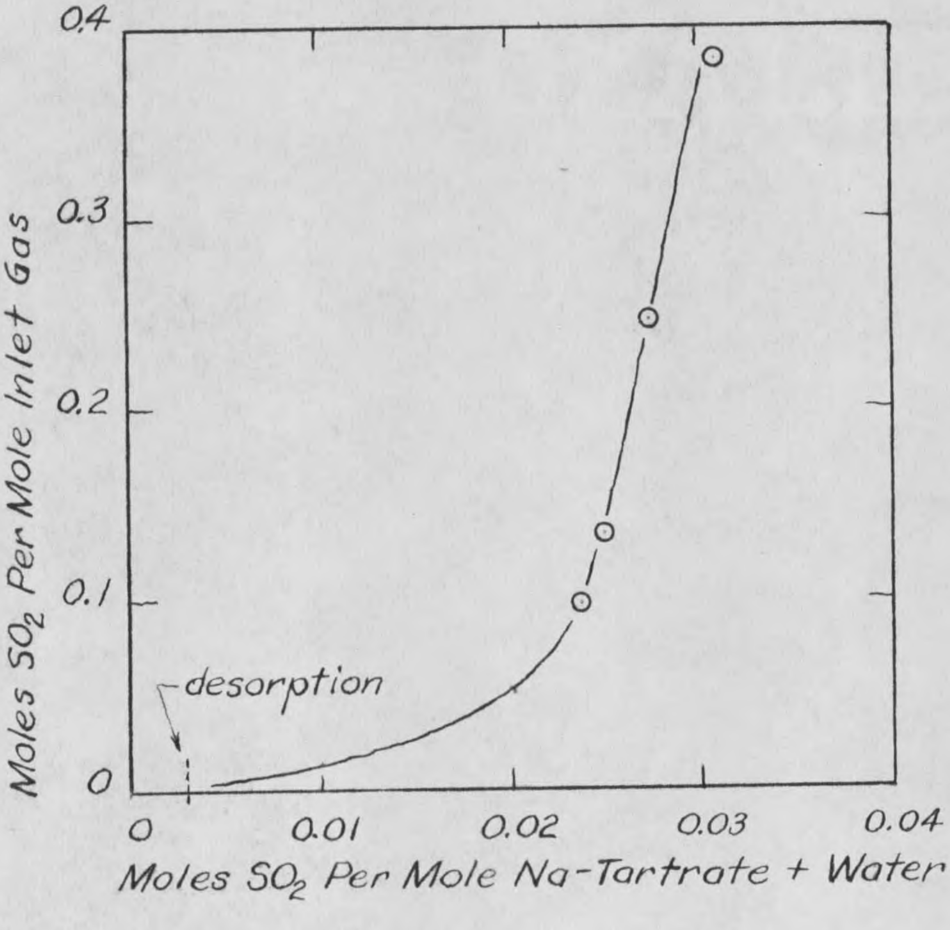

Figure 7. Equilibrium curve of sodium tartrate.

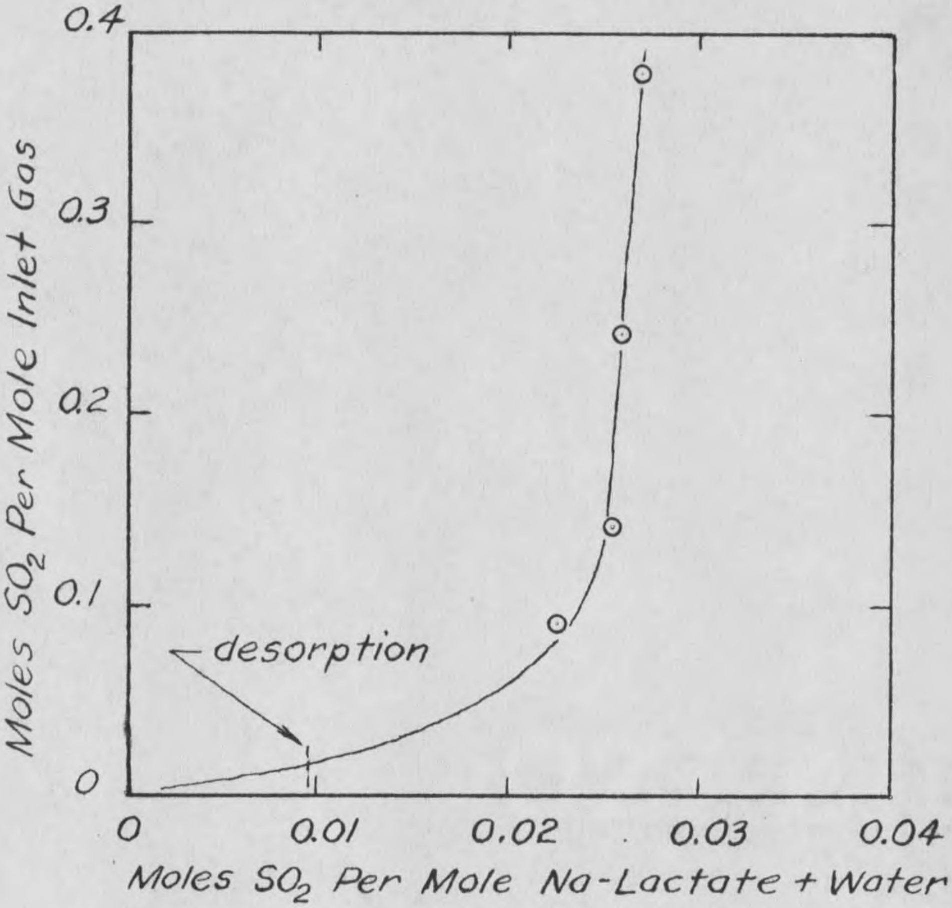

Figure 8. Equilibrium curve of sodium lactate.

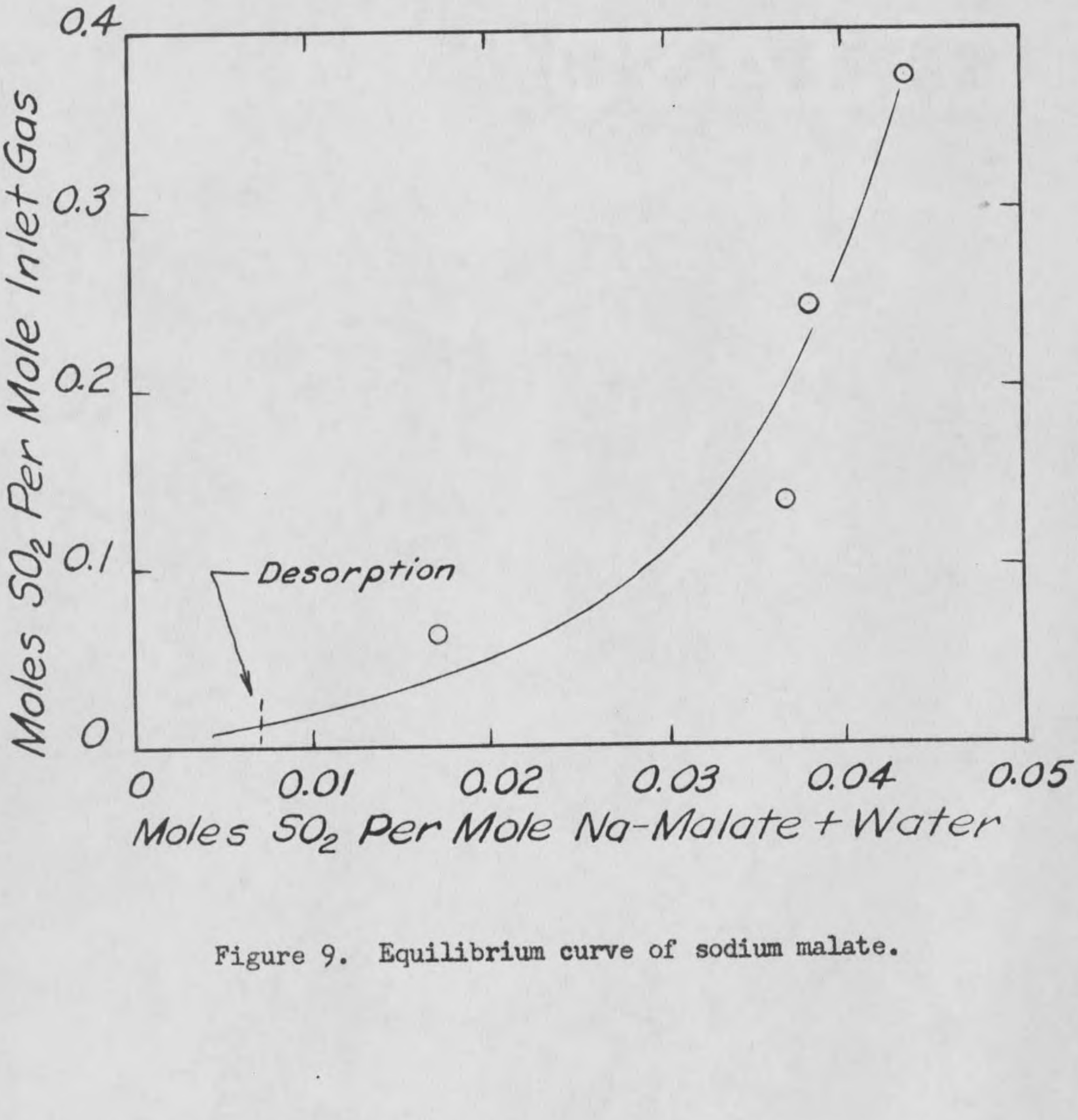

Figure 9. Equilibrium curve of sodium malate.

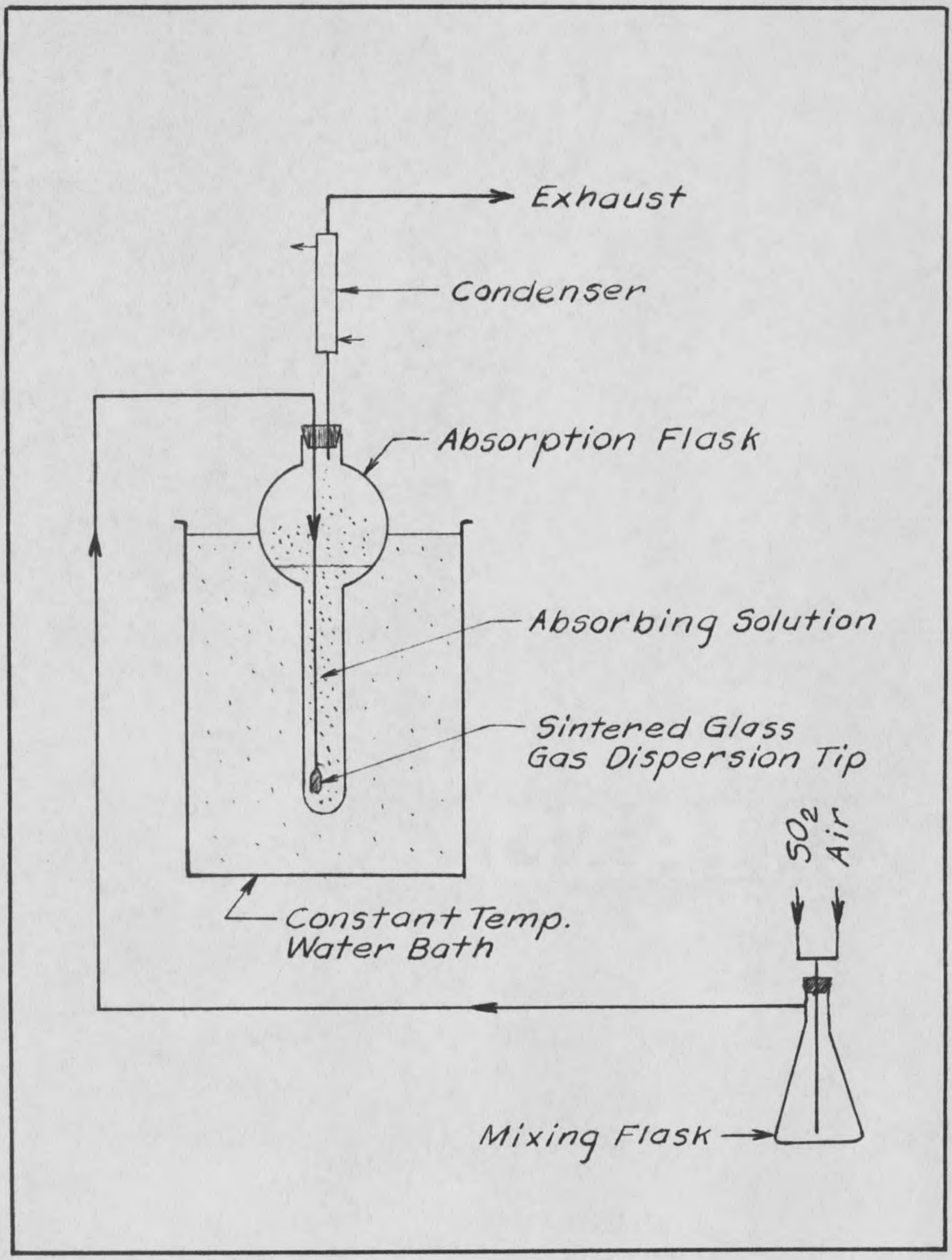

Figure 10. Apparatus for Equilibrium Curve Determinations

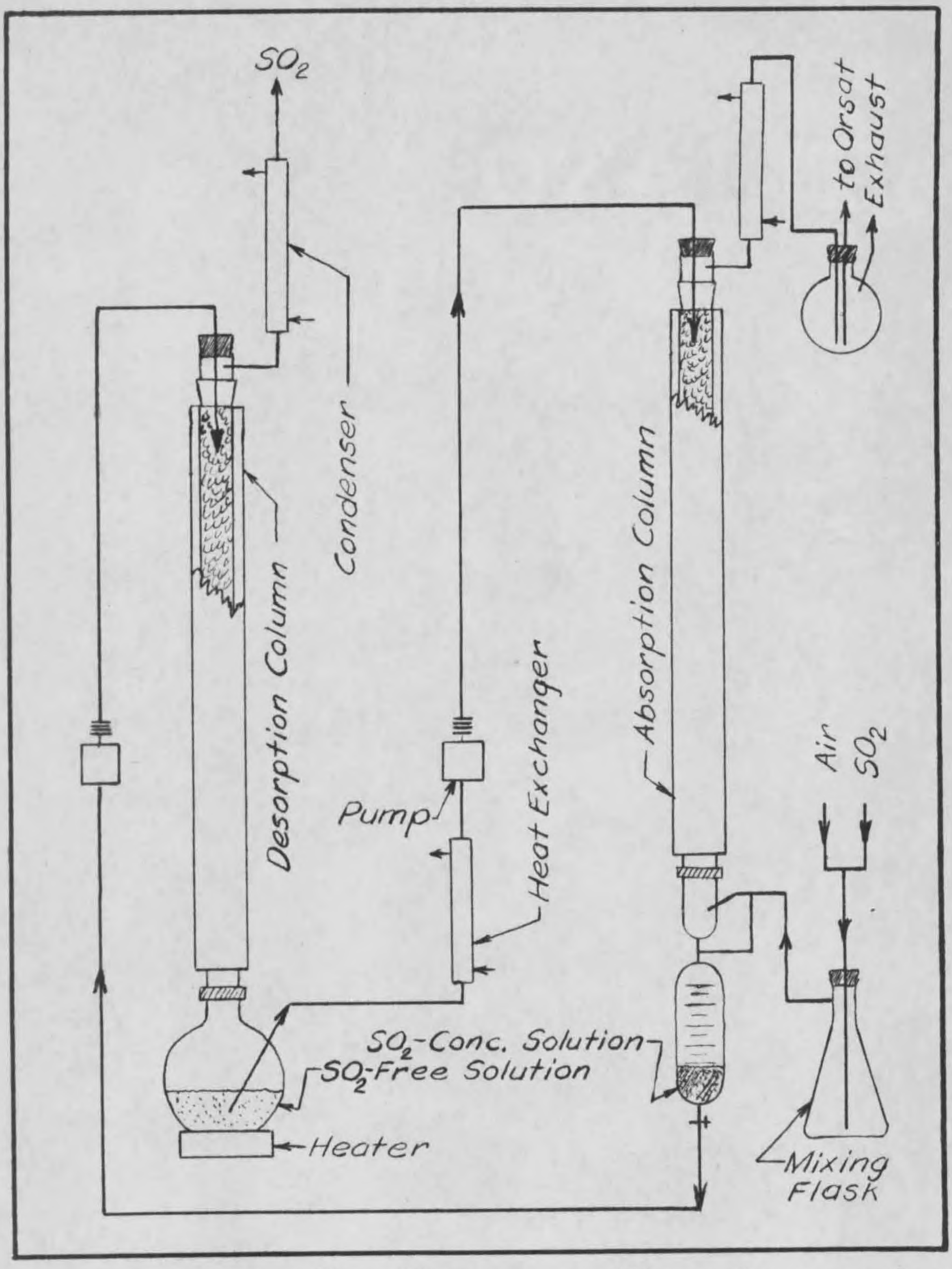

Figure 11. Continuous-Flow Apparatus Diagram

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Damon, R. A. 129759
Concentration of sulfur
dioxide from industrial
waste-gases.

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